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# Synthesis of Emissive Water-Soluble Network Polymers Based on Polyhedral Oligomeric Silsesquioxane and Their Application as an Optical Sensor for Discriminating the Particle Size

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**Keyword:** POSS, Network polymer, Hybrid gel, Silica particle, Fluorescence, Optical sensor

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## ABSTRACT

We report organic–inorganic hybrid gels composed of polyhedral oligomeric silsesquioxane (POSS)-based network polymers and their variable emission properties depended on the size of coexisting silica particles (SPs). The POSS networks were constructed from octaammonium POSS by connecting with bithiophene dicarboxylic acid. By modulating the feed ratio of the bithiophene linker, the series of the POSS networks were obtained with various cross-linking ratios among the POSS units. The POSS networks showed good water-solubility and emissions originated from the bithiophene linkers in water. Initially, it was observed that the POSS networks with relatively-lower cross-linking ratio showed the higher affinity to SPs. The increase of the affinity was observed from all POSS networks to the small-sized SPs. Interestingly, it was found that the emission properties were varied simply by adding the silica particles into the sample. In the presence of the nanoparticles dispersed in the sample, the red-shifted emission of the POSS network was induced. On the other hand, the blue-shifted emission was observed from the samples containing the microparticles. These peak shifts depended on the size of coexisting particles should originate from the polarity changes around the bithiophene cross-linkers induced by the adsorption of the POSS networks onto the particle surfaces. These emission characteristics could be applicable for developing a facile optical chmosensor for discriminating the size of the nanomaterials.

## Introduction

In nanotechnology, it is essential to clarify the shape of the synthesized nanomaterials. For example, the semiconductive nanocrystals show colorful emissions originating from the quantum confinement.[1a] To explain their optical properties, it is necessary to determine the size of each crystal at the nano-meter scale.[1b] As another example, the nanostructured materials have been used as a scaffold for constructing the chemical sensors.[2] In particular, their structural features were advantageous such for improving the sensitivity on the detection.[2] Therefore, it is proposed that the design of a chemical sensor based on the nanomaterials is promised to be the valid strategy for realizing the facile detection of nano-structured substances. The microscopic observation enables us to have direct information on the particle morphology. Size, shape, surface roughness, assembling, and ordering of the particles can be clearly visualized.[1c-1d] By using the light-scattering method, the particle radii can be estimated from the dispersion as the values involving the solvation molecules. In polar solvents such as water, the solvation effect often plays a critical role in their behaviors or functions. The light-scattering method provides the significant information involving solvation and aggregation.[1e] Both methods are conventionally used for the characterization of the nanoparticles. However, large-sized precise instruments are necessary for the observations with above methods. In addition, to receive reliable values, the pretreatment of the observation samples should be necessary.

An optical sensor is one of simple and versatile tools for target detection. Only by mixing with the probe which can change the optical properties by recognizing the target materials, not only the existence but also much detailed information on the target can be obtained.[3] Stimuli-responsive emissive materials are a suitable platform for constructing optical sensors. By modulating the recognition unit, the detection target can be tuned. So far, various types of optical sensors are applied in a wide variety of fields.[4] Nano to micro-sized particles have

been recently paid much attention as a pollutant in atmosphere. In particular, it has been reported that some size range of the particles showed critical bio-activity.[5] Therefore, the facile method for discriminating the existence and the morphology of particles is required. However, there are very few examples, to the best of our knowledge, to offer the optical sensors for detecting the nanoparticles. It is challenging to develop the probe materials for monitoring the size of the particles simply by the change in the emission properties of the probe.

Polyhedral oligomeric silsesquioxane (POSS) derivatives have attracted attention as a building block for constructing functional materials.[6] We have recently reported organic–inorganic hybrid gels composed of the network polymers containing polyhedral oligomeric silsesquioxane (POSS).[7] In particular, it was shown that the water-soluble POSS-containing materials such as dendrimers[7a–f] and network polymers[7g–i] can efficiently encapsulate hydrophobic guest molecules. According to the results from the survey with the polarity-sensing dye for the internal circumstances of the above POSS polymers, it was revealed that the POSS units can maintain the distinct hydrophobic spaces in the aqueous media.[7b,7g] Because of this strong hydrophobicity of the POSS unit, guest molecules were adsorbed to POSS. As a result, apparent water-solubility of the guest molecules can be improved by the encapsulation. More recently, it was found that hydrophobic spaces around the POSS unit can enhance the complex formation via the hydrogen bonds.[7b,7i] The selective encapsulations for bio-significant molecules into the POSS-containing dendrimers[7b] and network polymers[7i] were accomplished. Our next challenge is to apply the POSS networks as a recognition unit for nano-sized substances. We aimed to develop the optical sensor for the particles with the adsorption to the POSS unit. Herein, the water-soluble POSS networks with the sensing ability for the size of particles are presented. Due to the conjugated cross-linking unit, the synthesized POSS networks showed strong emission in aqueous phase. Especially, it was

demonstrated that the emission properties of the POSS networks can be modulated by changing the size of coexisting silica particles (SPs) from nano to micro size. Based on this change, the optical sensors for discriminating the particle size were obtained.

## Experimental Section

**General.** Octa-substituted ammonium POSS (Amino-POSS)[7h], bithiophene dicarboxylic acid[8], 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)[9] and silica particles (SPs)[10] were prepared according to the previous reports. Triethylamine ($Et_3N$), hydrochloric acid (HCl), deuterium oxide ($D_2O$), dimethyl sulfoxide (DMSO) and methanol were obtained from Wako Pure Chemical Industries, Ltd. DMSO-$d_6$ was obtained from Merck & Co., Inc. Deionized water was purified with an Autopure WEX3 system from Yamato Scientific Co., Ltd. Other reagents were used as received.

**Measurements.** $^1$H NMR and $^{13}$C NMR spectra were measured with a JEOL EX-400 (400 MHz for $^1$H, 100 MHz for $^{13}$C) spectrometer. $^{29}$Si NMR spectra were measured with a JEOL JNM-A400 (80 MHz) spectrometer. Coupling constants ($J$ value) are reported in Hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using residual dimethyl sulfoxide ($\delta$ = 2.50 in $^1$H NMR, $\delta$ = 39.5 in $^{13}$C NMR) as an internal standard. Emission from the samples was monitored using a Perkin Elmer LS50B at 25 °C using 1 cm path length cell. The dynamic light scattering (DLS) measurements were carried out at 90° scattering angle and 25 ± 0.2 °C using a FPAR-1000 particle analyzer with a He-Ne laser as a light source. The CONTIN program was used for data analysis to extract information on the average hydrodynamic size. MASS spectra were obtained on a JEOL JMS-SX102A.

**Preparation of POSS network.** A typical procedure is shown here: Bithiophene dicarboxylic acid (29 mg, 0.11 mmol) was dissolved in 5 mL DMSO with 10 mL Schlenk flask under argon atmosphere. Triethylamine (22 $\mu$L, 0.45 mmol) and DMT-MM (63 mg, 0.23 mmol) were added to the solution, and the mixture was stirred at room temperature for 1 h under Ar. Amino-POSS (50 mg, 0.057 mmol) was added slowly to the mixture, and the

solution was stirred at room temperature for 3 days under Ar. The mixture was changed from a suspension to a clear solution. After stirring, the solution of the mixture was dropped to 30 mL of cold methanol contained 0.1 wt% HCl. The precipitation was collected by centrifugation and was washed with methanol three times for removing non-reacted POSS and fragmented gels. The strained powder was dissolved in 10 mL of deionized water, and then the aqueous solution was filtrated to remove insoluble products. The aqueous solution was evaporated and dried *in vacuo* to give the POSS network polymer cross-linked with bithiophene dicarboxylic acid. $^{1}$H NMR (Figure S1, 400 MHz, $D_2O$, 25 °C): δ 7.49 (b, 2H, $C_{4,4'}H$), 7.26 (2H, $C_{3,3'}H$), 6.87 (2H, N*H*), 2.89 (2H, −C$H_2$−NH−), 1.65 (2H, −C$H_2$−C$H_2$−), 0.59 (2H, −C$H_2$−Si−). $^{29}$Si NMR (Figure S2, 80 MHz, DMSO-$d_6$, 25 °C): δ –66.15.

**Measurement of absorption properties.** Absorption properties of POSS network cross-linked by bithiophene were measured by peak top intensity of fluorescence emission spectra. Samples (0.5 mL) containing POSS-BT(*n*)s (0.5 mg/mL) and SPs (0.5 mg/mL) were prepared by mixing the same volumes of the stock samples (1 mg/mL). Then, the series of measurements were performed. In summary, 250 μg of particles was used for the optical measurements.

## Results and Discussion

The design and preparation of the materials are shown in Scheme 1. To obtain emissive materials, we designed the POSS networks with the bithiophene cross-linker. It was reported that bithiophenes show the different emission properties under various polarity environments.[8a] According to these emission changes, we expected that the emission property of the bithiophene moiety could be altered by the adsorption of the POSS networks onto the target particles. Moreover, it was shown from our previous results that the internal hydrophobicity of the POSS networks should be enhanced by increasing the cross-linking ratio because the ionic ammonium groups were transformed to the amide groups although the water-dispersibility was lowered.[7h] Therefore, it is presumed that the increase of the cross-linking ratio in the network should be favorable for improving the affinity to the particle. Bithiophene dicarboxylic acid[8] was reacted with octa-substituted ammonium POSS (Amino-POSS)[7h] in the presence of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)[9] as a condensation reagent. We prepared the series of the POSS networks with various cross-linking ratios by modulating the feed ratios of bithiophene dicarboxylic acid to Amino-POSS (Table 1). In the abbreviation, *n* denotes the mol% of POSS-BT(*n*) toward Amino-POSS in the feed ratio. The products had good solubility in water. From $^{1}$H NMR spectra, the cross-linking ratios between the POSS units were determined. The formation of the silica cube was confirmed by $^{29}$Si NMR spectra. The clear $^{13}$C NMR signals were not obtained from the products because of low molecular motions of the POSS networks. From DLS, the larger sizes of hydrodynamic radii ($r_H$) were obtained compared to that of Amino-POSS. From these characterization data, we concluded that the POSS network polymers were obtained. SPs were prepared according to the Stöber method.[10] From TEM observations, the particle sizes were calculated as an average with 100 particles (Figures S3 and S4). We obtained various sizes (0.04 nm ~ 1.5 $\mu$m) of SPs with low size

distributions. We also prepared bithiophene diamide as a model compound of the linker moiety.

Scheme 1 and Table 1

Basic optical properties were examined with the materials used in this study. Initially, the optical measurements were performed in the solution state. In the absorption spectra, the characteristic band with the peak at 350 nm attributable to π-π* transition in the bithiophene linker was observed from the POSS networks (Figure 1a). Comparing to the spectra of the model compounds as bithiophene dicarboxylic acid and bithiophene diamide, significant peak shifts were not detected. This result means that the formation of amide bonds at both carboxyl groups should hardly influence on the electronic structure of bithiophene in the ground state. Even in the presence of the SPs (1.5 $\mu$m), the absorption peak was observed at the same position although the background level was elevated by light scattering. These data indicate that the absorption properties of the bithiophene linker should be maintained in all situations. In the further experiments for recording the emission, all samples were irradiated with 350 nm wavelength light for the excitation.

Figure 1

Figure 1b represents the emission properties of the materials in the solution state. In the spectra, the emission bands were observed with the peaks at 406 nm from both bithiophene dicarboxylic acid and bithiophene diamide. This fact means that the chemical modification should hardly influence on the emission property of the ligand. On the other hand, by connecting to POSS, the bathochromic shift of the emission band was observed by 30 nm. In

the previous reports, bathochromic shifts of the bithiophene derivatives were presented.[8] In the solutions containing bithiophene and acetyl bithiophene, the bathochromic shifts can be induced by adding the low polar polymers.[8] Similarly, the POSS network could provide the strong hydrophobic spaces around the bithiophene linker. As a result, the red-shifted emission was obtained from the POSS network.

We investigated the adsorption behavior of the POSS networks to SPs. To evaluate the amount of the POSS networks adsorbed onto the surface of particles, the emission intensities of the solution containing the POSS networks were compared with that of the supernatant after SPs addition and following centrifugation (Figure S5). From the decrease of the emission intensity, we calculated the linker concentration from the integration of the emission bands in the spectra (Figure 2). The emission intensities of the POSS-BT(1) solutions critically decreased by adding all sizes of SPs (Figure 2a). POSS-BT(2) showed the variable adhesion ability toward the particle size (Figure 2b). Efficient adhesion was observed to SPs with 0.04 nm. The adsorption was slightly observed to relatively-larger sizes of SPs. On the other hand, slight changes in the emission intensity were observed with POSS-BT($n$) ($n$ = 3 and 4) in the presence of SPs (Figures 2c and 2d). These data indicate that POSS-BT(1) can be adsorbed onto the surfaces of SPs regardless of particle size, while POSS-BT($n$) ($n$ = 3 and 4) should be hardly adsorbed to SPs. According to the DLS data, the POSS network with higher cross-linking ratio showed smaller $r_H$ value. This result suggests that the increase of cross-linking ratios could induce the condensation of the network structure, and the flexibility should be lost. It is likely that the adhesion should be disturbed because of the decrease of adhesion area by the condensation of the network. In addition, by increasing the particle size, the surface area should decrease. As a result, the amount of the adhesion could be reduced. Once after adsorbing onto the surfaces of SPs, the POSS networks were tightly immobilized.

Moreover, the preparation cost of the POSS network is low. Therefore, the POSS networks could be applicable such as a disposable high-efficiency particulate air filter.

Figure 2

The influences of the emission properties of the POSS networks before and after adhesion were monitored. The solution containing 1 mg/mL of POSS-BT(2) presented the emission band with the peak at 436 nm. Interestingly, in the presence of the SPs (1.0 $\mu$m), the blue-shifted emission band by 17 nm was observed (Figure 1b). By decreasing the particle size of SPs, the degree of the peak shift decreased. In contrast, the bathochromic shift of the emission was obtained in the presence of the smaller size (ca. 40 nm) of SPs (Figure 3c). The optical properties of POSS-BT(2) were modulated by the size of coexisting SPs.

Figure 3

To gather the informations on the changes of the emission properties of SPs, we performed the same experiments with the POSS networks with different cross-linking ratios (Figure 3). POSS-BT(1) which has the lowest cross-linking ratio and the largest adsorption ability in the synthesized polymers presented the red-shifted emission band in the presence of all SPs (Figure 3a). By increasing the cross-linking ratio, the blue-shifted emission bands were obtained in the presence of relatively-larger sizes of SPs. POSS-BT(1.5) and POSS-BT(2) showed the blue-shifted spectra by 6 nm and 15 nm in the presence 1.5 $\mu$m SPs, respectively (Figures 3b and 3c). The less significant peak shifts were obtained from the POSS networks with larger cross-linking ratios by adding all sizes of SPs (Figures 3d−3f). According to the adsorption experiments, the amounts of the adhesion of the gels onto the surface of SPs

decreased. It is likely that the small interaction between the gels and SPs induces less influence on the emission spectra.

The changes in the emission properties by the addition of SPs can be explained by the adsorption behaviors of the POSS networks to the particle surfaces. In the spectrum of POSS-BT(2) in the presence of the small-sized SPs, the red-shifted emission was obtained. The adsorption and closely assemble of the linker units at the surface of SPs should occur mediated by the strong interaction between POSS and particle surfaces. Consequently, the hydrophobicity around the linker units could be enhanced, resulting in the observation of the red-shift emission (Figure 4). Whereas, in the presence of the larger size of SPs, the blue-shifted emission was obtained as observed from the sample with POSS-BT(2) and larger-sized particles. From the adsorption evaluation, it was observed that the relatively-weaker interaction to SPs occurred. Comparing the peak positions of the emission bands with the POSS networks, it was found that bithiophene dicarboxylic acid intrinsically presented the blue-shifted emission. From these data, it is assumed that the linker units could be relatively isolated from the POSS core in the presence of the larger size of SPs (Figure 4). The POSS moiety could be preferentially adsorbed onto the particle surface. Finally, the linker moiety could be enforced to the free spaces. These speculation can be supported by the emission decay measurements (Figure 5). The shorter decay time was observed from the sample in the presence of SPs than that in the absence of SPs (Table 2). In POSS-BT(2), the molecular motions of the bithiophene linker should be suppressed by POSS. Thereby, the lifetime at the excited state was elongated. On the other hand, in the presence of SPs, only the POSS unit was adsorbed onto the particle surfaces, and the bithiophene units could have the flexibility in the rotation. Thereby, the decrease of the decay time could be obtained. Finally, the similar emission spectra to the solution state were observed from the POSS networks. To evaluate the detection limit of our system, the influence of the SP concentration on the degree of peak

shifts in the emission spectra (Figure S6). Accordingly, the size discrimination was achieved with 25 $\mu$g (0.05 mg/mL) of SPs (1.5 $\mu$m) with POSS-BT(2). This sensitivity is enough for monitoring the silica nanoparticle-based molecular probes.[12]

Figures 4 and 5, Table 2

## CONCLUSION

We demonstrate the preparation of emissive organic−inorganic hybrid gels with POSS and their discrimination ability of the size of SPs. By the adhesion of the POSS networks to the particle surface, the peak positions in the emission spectra were shifted. Based on these changes, we finally obtained the signal responses for discrimination of the size of the particles from the optical property. If only several hundred micrograms of SPs are obtained, we can readily estimate the size by measuring the peak position in the emission spectra from the dispersion of the sample in the presence of the POSS networks. We show the degree of adhesion to the particle surfaces can be tuned by modulating the cross-linking ratio in the POSS networks. These characteristics might be also applicable for developing the chemosensor for the shape of the nanomaterials except for the particles.

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**Scheme 1.** Synthesis of the POSS networks

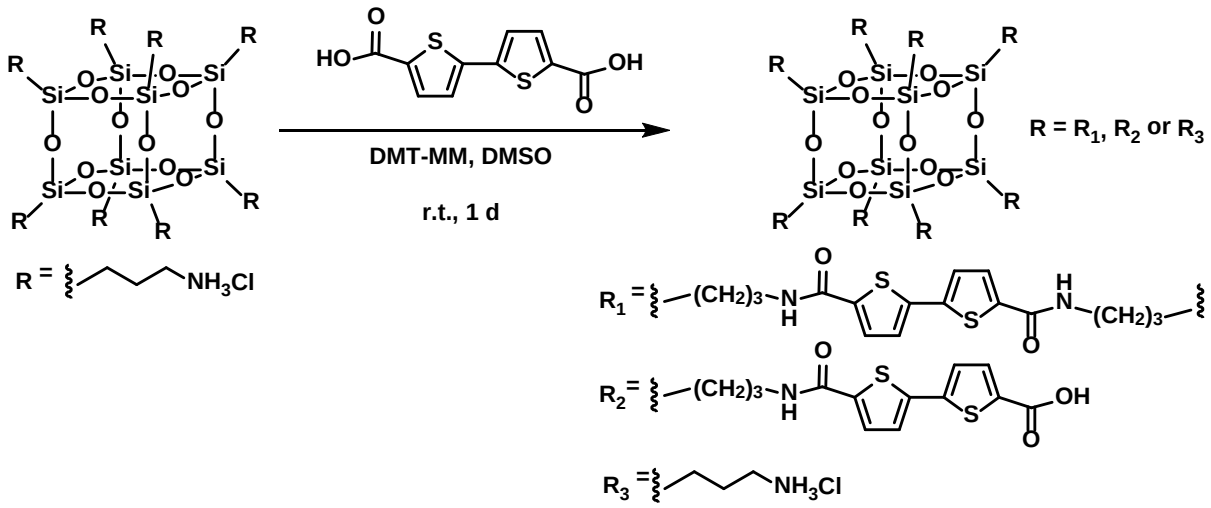

**Table 1.** Physicochemical properties of the POSS networks

| Polymer | Feed ratio of dicarboxylic acid (eq.) | Yield (%) | Crosslinking Ratio (%)[a] | $r_H$ (nm) | $\lambda_{abs,max}$ (nm) | $\lambda_{em,max}$ (nm) | $\Phi_{PL}$[b] |
|---|---|---|---|---|---|---|---|
| POSS-BT(1) | 1.0 | 84 | 6.9 | 371 ± 35 | 350 | 413 | 0.059 |
| POSS-BT(1.5) | 1.5 | 64 | 10 | 136 ± 36 | 350 | 422 | 0.057 |
| POSS-BT(2) | 2.0 | 54 | 13 | 116 ± 17 | 350 | 433 | 0.073 |
| POSS-BT(2.5) | 2.5 | 58 | 14 | 91 ± 10 | 350 | 420 | 0.048 |
| POSS-BT(3) | 3.0 | 86 | 25 | 53 ± 17 | 350 | 413 | 0.041 |
| POSS-BT(4) | 4.0 | 52 | 36 | 43 ± 7 | 350 | 413 | 0.051 |

[a]All values were determined from the $^1$H NMR spectra.

[b]Calculated as a relative value toward the absolute value of POSS-BT(2).

**Table 2.** Decay times of the POSS networks

| | $\tau$ (ns) |
|---|---|
| Bithiophene dicarboxylic acid | 0.43 |
| POSS-BT(2) | 6.0 |
| POSS-BT(2)+SPs[a] | 4.5 |

[a] 1.5 $\mu$m diameter.

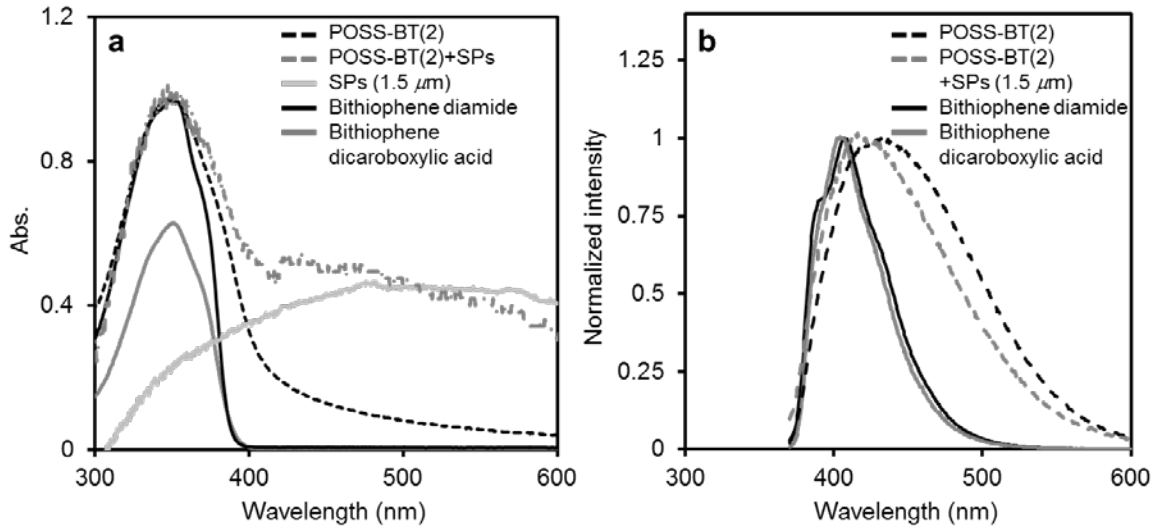


**Figure 1.** (a) Representative UV−vis absorption spectra of the samples containing $5 \times 10^{-6}$ M each compound with or without 0.5 mg/mL of SPs. The spectra of POSS-BT(2) were fitted to that of bithiophene diamide. (b) Normalized photoluminescence spectra of the compounds with the excitation light at 350 nm.

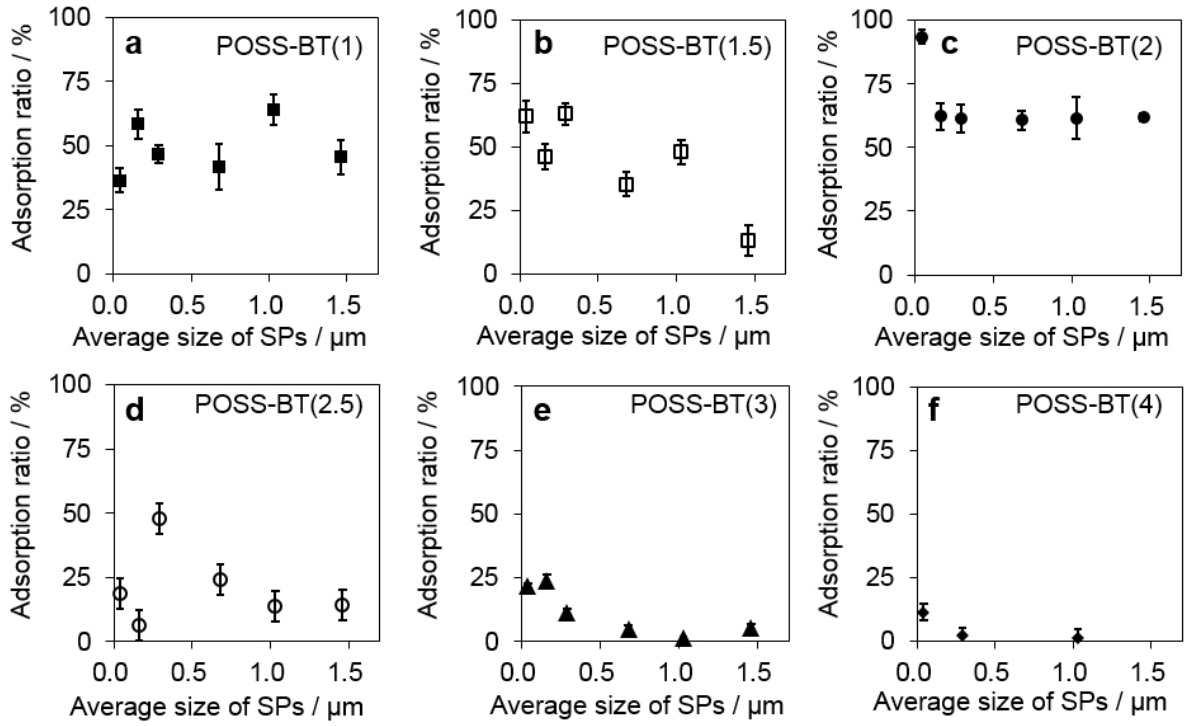


**Figure 2.** The amounts of the adsorbed POSS networks on the particle surface in the samples containing 0.5 mg/mL of POSS-BT(n) in the presence of various sizes of SPs (0.5 mg/mL).

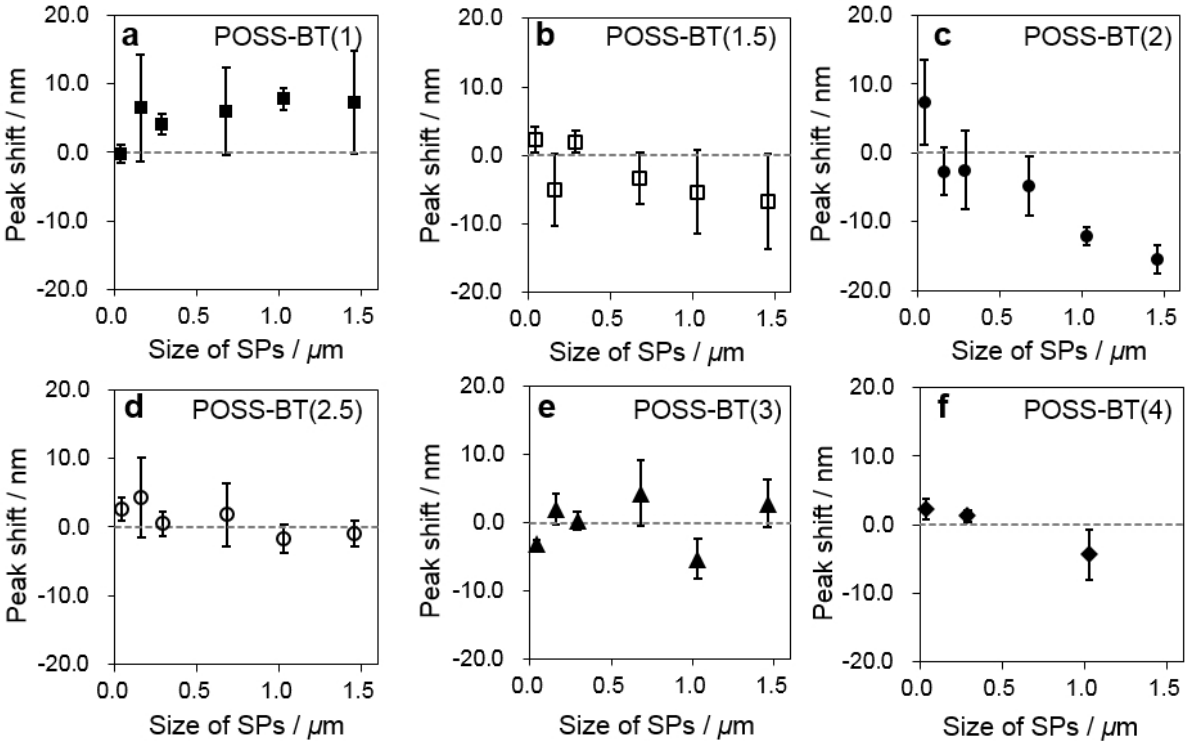


**Figure 3.** The degree of the peak shifts of the emission bands from POSS-BT(*n*)s by adding various size of SPs.

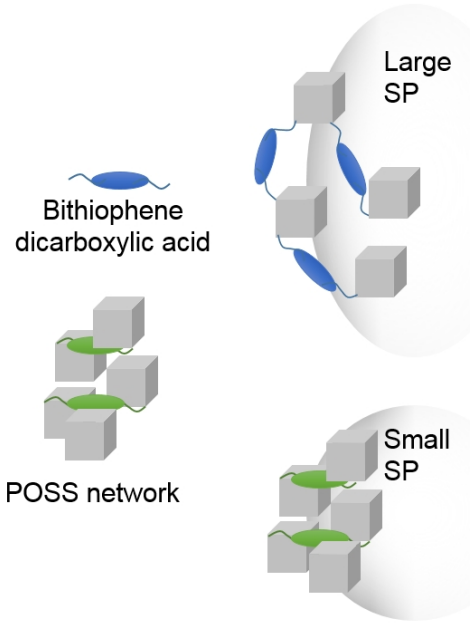


**Figure 4.** Plausible models of the blue-shifted emission from the POSS network in the presence of SPs.

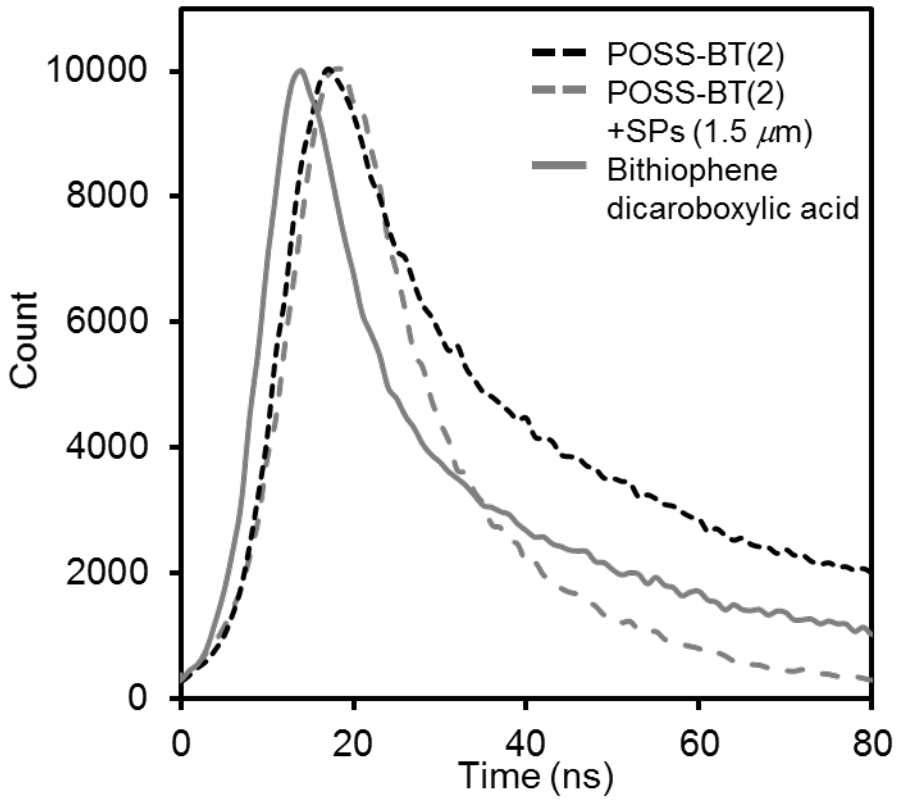


**Figure 5.** Fluorescence decay curves of bithiophene dicarboxylic acid, POSS-BT(2), and the mixture with POSS-BT(2) and SPs (1.5 $\mu$m).

## Graphical Abstract: